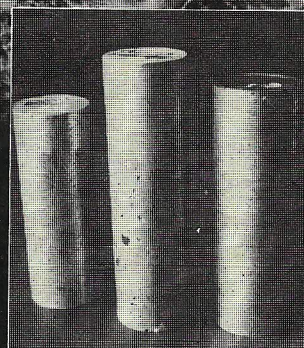
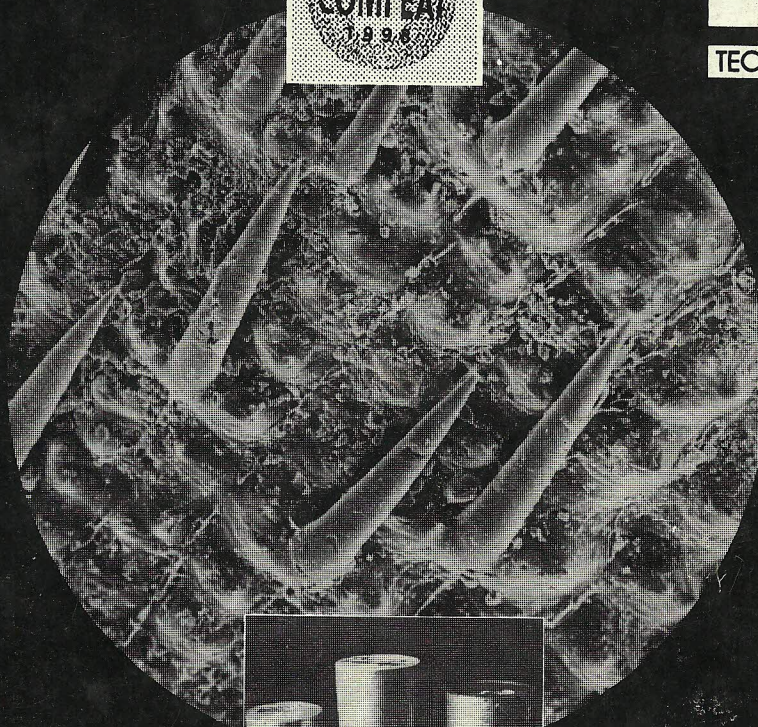


PROCEEDINGS

# COMPOSITE MATERIALS

MANUFACTURE  
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# PREPARATION OF $\text{Al}_2\text{O}_3$ - $\text{SiC}_w$ IN-SITU COMPOSITE POWDER MIXTURES BY CARBOTHERMAL REDUCTION OF KAOLINITE

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## Abstract

$\text{Al}_2\text{O}_3$ - $\text{SiC}_w$  composite powder mixtures were prepared by carbothermal reduction of kaolinite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) in argon atmosphere at constant gas pressure of 0.15 MPa. The reactions were carried out with different mole ratios of silica (in the precursor) and carbon (4.5-9.0), with two types of carbon i.e. carbon black ( $300\text{m}^2/\text{g}$ ) and activated charcoal ( $1000\text{m}^2/\text{g}$ ) and at different temperatures in the temperature range of 1550-1700°C with one hour of soaking to find the progress of the reaction in all the cases. It was observed that the reactions were complete at 1700°C. The reactions were carried out with higher soaking time to optimise the process. It was noted that mullite forms as the intermediate phase at lower temperatures which converts progressively later to a mixture of  $\text{Al}_2\text{O}_3$  and  $\text{SiC}_w$  composite product at higher temperatures.

## Introduction

The mechanical properties such as strength and toughness of monolithic ceramic materials e.g.  $\text{Al}_2\text{O}_3$ ,  $\text{Si}_3\text{N}_4$ ,  $\text{ZrO}_2$  etc. can be increased by introduction of a second ceramic phase in the form of whiskers. For example  $\text{Al}_2\text{O}_3$  -  $\text{SiC}$  whisker composites possess better room and high temperature strengths and toughness as compared to monolithic alumina [1,2]. In addition, these composites display high resistance to thermal shock and to high temperature creep [3,4].

The composite bodies which are prepared generally by physical mixing of the matrix powders like  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  or  $\text{Si}_3\text{N}_4$  etc. with  $\text{SiC}$  whiskers are not homogeneous due to the shape and size mismatch of the whiskers and the matrix materials resulting in an inhomogeneous distribution of the  $\text{SiC}$  whiskers in the matrix phase. The whiskers also give rise to self agglomeration and interlocking (like woolen balls) problems. The whiskers are expensive since they are prepared from costly organic precursors. On the other hand in-situ preparation of whiskers by carbothermal reduction of alumino-silicates is anticipated to be a simple process which is very cheap and provide better homogeneity and dispersion of  $\text{SiC}$  whiskers. For example, the



carbothermal reduction reaction of kaolin has been studied most extensively by various workers [5,7]. In this study, the effect of various reaction parameters e.g. temperature (1550-1700°C), the mole ratio of carbon to silica (4.5-9.0), nature and source of carbon (activated charcoal or carbon black) on the carbothermal reduction of kaolin is presented.

### Experimental Procedure

Kaolinite powder (M/s English India Clays, India) with a particle size distribution as shown in Fig. 1 was directly used as the precursor for the reaction. Activated charcoal (M/s S.D. Fine Chemicals, India) and carbon black (M/s Degussa, Germany) possessing B.E.T. surface areas of 1000 and 300 m<sup>2</sup>/g respectively with 4.5, 5.5 and 9.0 moles of carbon per mole of silica content in kaolinite were mixed in ethyl alcohol medium. After a good mechanical agitation for 30 minutes the alcohol was evaporated to obtain homogeneous powder mixtures. The powders were loaded into graphite crucibles whose lids contained small holes for the precursor powders to communicate and equilibrate with the outside furnace atmosphere at high temperatures. The crucibles and their lids after charging with the powders were initially sealed with an organic resin (Araldite, M/s Ciba Geig, India) and placed in the hearth of a graphite furnace with internal graphite heating elements inside a carbon-carbon composite fibre board insulation. The furnace chamber containing the reactant crucibles was then evacuated to milli bar and back-filled with high purity argon gas to a positive pressure of 0.15 MPa. The temperature inside the furnace was measured by a bare W-5%Re/W-26%Re thermocouple. The furnace was equipped with an Eurotherm 414 thyristor powerpack and an Eurotherm 815 controller programmer to carry out the reactions at the desired temperatures and durations. The graphite furnace was heated in a programmed manner e.g., from room temperature to 1000°C at 10°C/min, from 1000°C to 1250°C at 5°C/min and finally from 1250°C to the desired temperature (e.g., 1550°C, 1600°C, 1650°C and 1700°C) at 3°C/min while the reacting masses were soaked for 1 hour in all cases, at the highest chosen temperatures. The product powders removed after the reaction were decarburised to get rid of excess unreacted carbon by heating in air at 700°C for 4 hours.

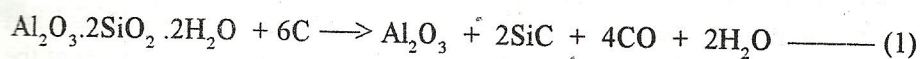
The products were subjected to X-ray diffraction (XRD) studies using CuK<sub>α</sub> radiation with nickel filters in a Rigaku X-ray diffractometer (M/s Rigaku Corp., Japan) for phase analysis. Scanning Electron Microscopy (SEM) was done in a JSM-35 Scanning Electron Microscope (M/s JEOL., Japan) for morphological analysis of the products obtained.

### Results and Discussions

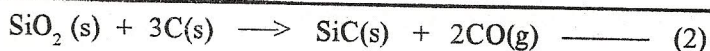
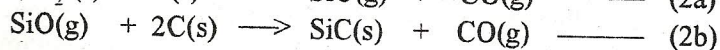
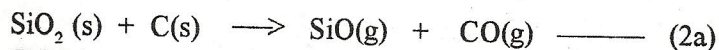
The overall chemical reaction of kaolinite with carbon (in an inert atmosphere



such as argon) can be stated as follows.



in which, silica part of the kaolinite would react with carbon to form SiC. The reaction of silica with carbon is known to proceed in the following two steps.



The reaction (2b) which is a solid - vapor reaction is known to be responsible for the formation of SiC mostly in whisker form. The morphology and the extent of reaction could be controlled by optimising various reaction parameters e.g. C:SiO<sub>2</sub> ratio, temperature and duration of the reaction. Due to the gaseous nature of SiO, the experiments are carried out in a closed reaction chamber with a positive gas pressure of (0.15MPa) of argon to minimise the loss of SiO gas from the crucibles. The reactions are carried out with loose powder mixtures with excess carbon for free whisker growth and completion of the reaction.

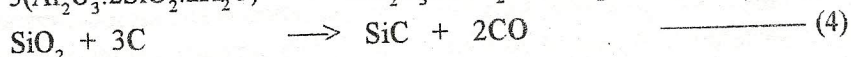
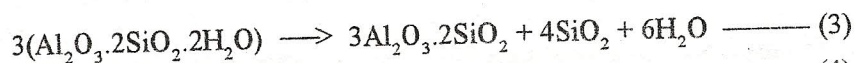
The product samples prepared under different conditions are designated by the following simple notation, e.g., KAC90A1650 denotes sample derived from kaolinite(K) precursors containing 9.0 moles of activated charcoal (AC) per mole of silica (in the precursor) in argon (A) atmosphere at 1650°C for 1hour. Typical XRD spectra of the products obtained in argon atmosphere at 1650°C and 1700°C using activated charcoal and carbon black (CB) of different mole ratios are presented in Fig.2(a - c) and in Fig 3(a - c) respectively. XRD patterns of all samples have been obtained taking a constant weight (100 mg) of the decarburised product, in view of which the peak height/the intensity of most intense non-overlapping peak of various species present in the product could be assumed to be representative of quantity of that particular species present in the product. The relative intensity of the most intense overlapping peaks of different species could therefore be assumed to be a measure of the extent of progress of carbothermic reaction under given set of experimental conditions. Thus peaks at 43.3° of 2θ (d = 0.2085nm) and 59.98° of 2θ (d = 0.1549nm) were taken as the representative (113) peak of α-Al<sub>2</sub>O<sub>3</sub> and (220) peak of β-SiC for monitoring the progress of the reactions respectively. The qualitative XRD analysis of various products are presented in Table 1.

An attempt was also made to broadly analyse the progress of the carbothermic reactions by evaluating the extent of formation of both α-Al<sub>2</sub>O<sub>3</sub> and β-SiC at the

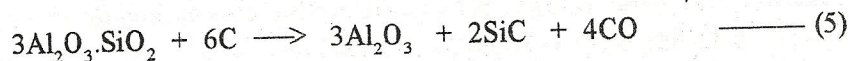


various temperatures of the reaction for different C:SiO<sub>2</sub> ratios. To illustrate the effect of carbon content on the reaction, intensity graphs of  $\beta$ -SiC (220) and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (113) peaks vs the number of moles of carbon used for the reaction were also plotted and these are presented in Fig.4(a-c). Typical SEM pictures of some of the products of the reaction are presented in Fig.5.

XRD patterns of samples reacted at 1550°C and 1600°C contain peaks of mullite, cristoballite and traces of  $\beta$ -SiC. This can be explained on the premise that kaolinite undergoes conversion to mullite and excess silica. A part of excess silica converts to  $\beta$ -SiC while the rest remains in the form of cristoballite at the low temperatures. The equation for the above two reactions are given below:



At 1650°C, presence of peaks of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in the XRD patterns of the products indicate that the reaction of mullite with carbon to form  $\beta$ -SiC and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has progressed as per the equation given below.



At 1700°C, the reaction was found to be complete in all cases. This was confirmed by absence of mullite in XRD patterns.

#### Effect of nature and amount of carbon

It is observed that the intensity of cristoballite decreases with increase in carbon content for both activated charcoal and carbon black. Hence it is concluded that higher mole ratios of carbon increases the reaction rate. The samples reacted with 9.0 mole ratio of activated charcoal show absence of cristoballite peaks at 1550°C and 1600°C while the corresponding samples containing carbon black show presence of cristoballite. It can be concluded that AC is more reactive than CB due to high surface area. The effect of number of moles of carbon on the reaction can be observed from the Fig.4. In case of both activated charcoal and carbon black, the reaction is complete for 4.5 and 9.0 mole ratios while it is nearly complete (presence of small peaks of mullite) in both the cases. This is due to the inhomogeneity during mixing at micro level.

#### Conclusion

It is concluded that carbothermal reduction of kaolin in argon produces Al<sub>2</sub>O<sub>3</sub> - SiC<sub>w</sub> composite powder. The rate of reaction is more for activated charcoal with higher



surface area and for higher carbon ratios. The morphology and whiskerisation is better for carbon black reacted samples.

### Acknowledgement

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### References

- 1) C.Wei and P.F.Becher, Am. Ceram. Soc. Bull., **64** (1985) 298.
- 2) T.N.Tiegs and P.F.Becher, Am. Ceram. Soc. Bull., **66** (1987) 339.
- 3) T.N.Tiegs and P.F.Becher, Am. Ceram. Soc. Bull., **70** (1987) C109.
- 4) A.H. Chokshi and J.R.Porter, J. Am. Ceram. Soc., **64** (1985) C144.  
J.R.Porter, F.F.Lange and a.H. Chokshi, Am. Ceram. Soc. Bull., **66** (1987) 343.
- 5) A.C.D. Chaklader, C.A.Das Gupta, E.C.Y.Lin and B Gutowski  
J. Amer. Ceram. Soc., **75** (1992) 2283.
- 6) S. Bandopadhyay and J.Mukherjee, Ceram. Int., **19** (1993) 133.
- 7) F.K.Van Dijen, C.A.M. Siskens and R.Metseller, "Science of Ceramics",  
Vol.12, Ed. Vincenzini, Ceramurga, s.r.l. Farenza, Italy, 1984, p.427.

**Table I**  
**Various product phases (analysed by XRD) at different reaction conditions**

Sl. No.	Reactants	C:SiO <sub>2</sub>	Product phases (as analysed by XRD) at Temp.			
			1550°C	1600°C	1650°C	1700°C
1.	Kaolin + AC	4.5	M, C, S	M, C, S	M, A, S	A, S
		5.5	M, C, S	M, C, S	A, S, M	A, S, M
		9.0	M, S	M, S	A, S, M	A, S
2	Kaolin + CB	4.5	M, C, S	M, C, S	A, S, M	A, S
		5.5	M, C, S	M, C, S	A, S, M	A, S, M
		9.0	M, C, S	M, C, S	A, S, M	A, S

AC = Activated Charcoal	CB = Carbon Black	M = Mullite
S = Silicon Carbide	C = Cristoballite	A = Alumina



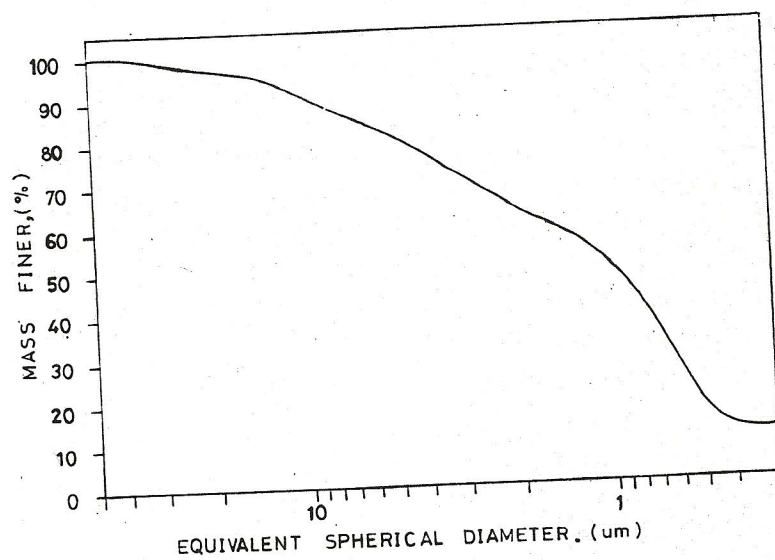


Fig. 1 - Particle size distribution of Kaolin.



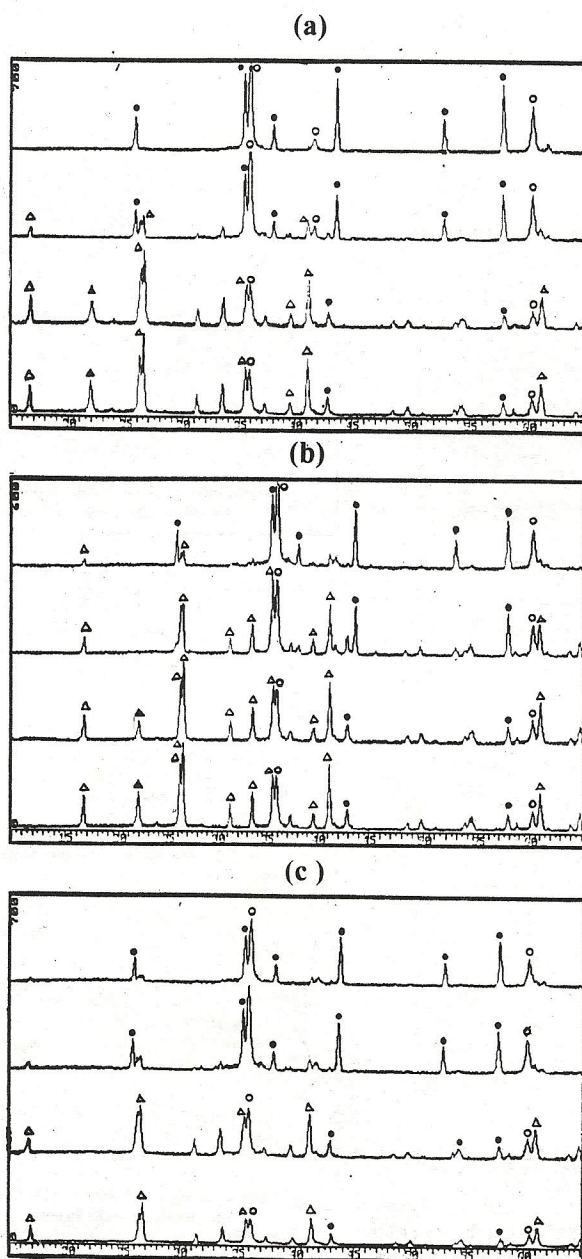


Fig. 2(a-c) - XRD patterns of the products obtained with (a) 4.5 (b) 5.5 (c) 9.0 mole ratios of activated charcoal at (1550° - 1700°C) from bottom to top respectively.

● :  $\alpha$ - $\text{Al}_2\text{O}_3$ , ○ :  $\beta$ - $\text{SiC}$ , △ : Mullite & ▲ : Cristoballite



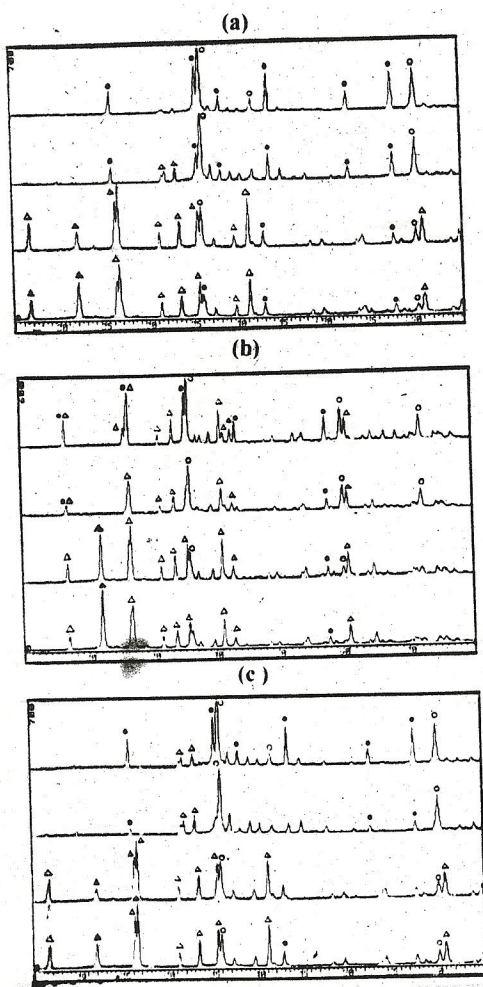


Fig. 3 (a-c) - XRD patterns of the products obtained with (a) 4.5 (b) 5.5 (c) 9.0 mole ratios of carbon black at (1550° - 1700°C) from bottom to top respectively.  
 ● :  $\alpha$ - $\text{Al}_2\text{O}_3$ , ○ :  $\beta$ -SiC,  $\Delta$  : Mullite &  $\blacktriangle$  : Cristoballite

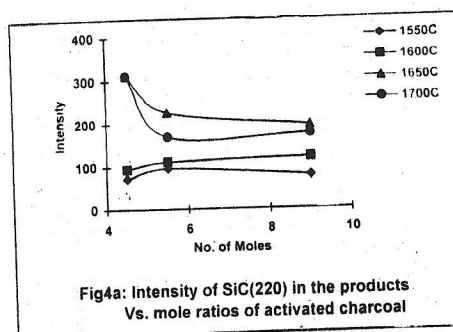


Fig4a: Intensity of SiC(220) in the products Vs. mole ratios of activated charcoal

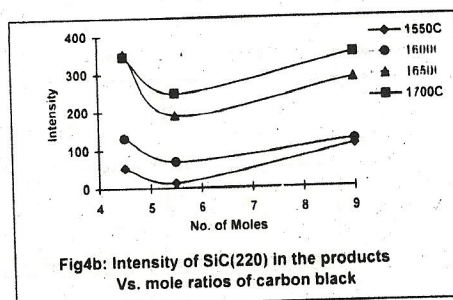


Fig4b: Intensity of SiC(220) in the products Vs. mole ratios of carbon black

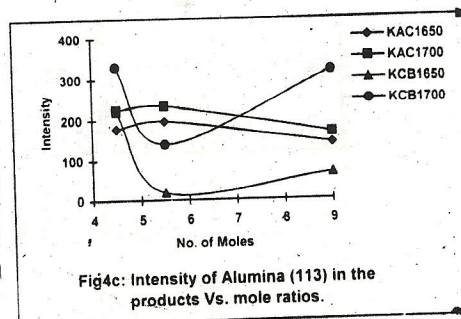


Fig4c: Intensity of Alumina (113) in the products Vs. mole ratios.



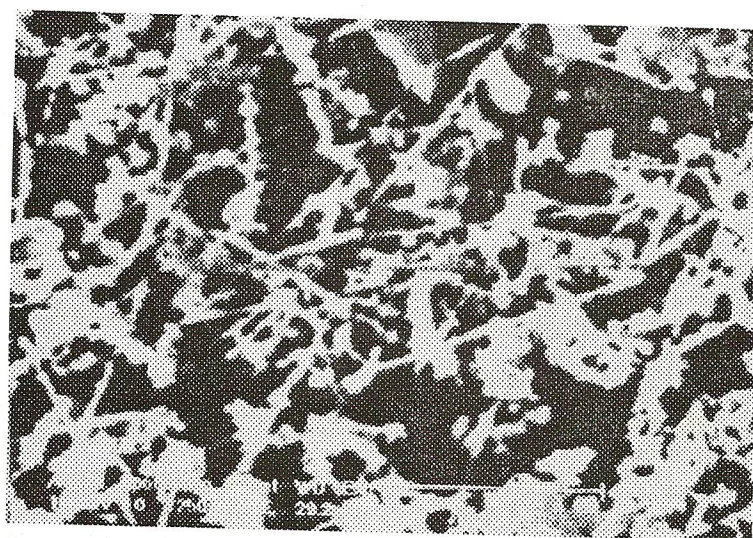
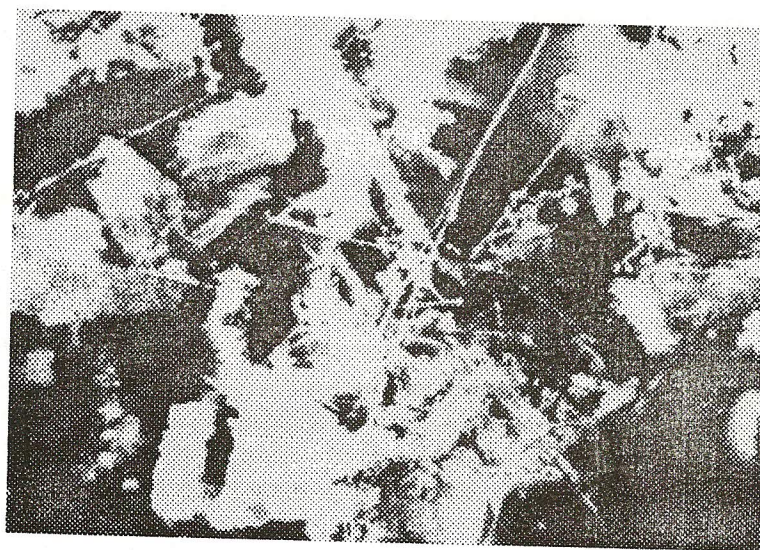


Fig. 5 - SEM pictures of products  
a) KAC55A 1700, X 2,500 b) KCB45A 1700, X 1,250